PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-087115

(43)Date of publication of application : 02.04.1996

(51)Int.Cl. G03F 7/11
G03F 7/004
G03F 7/004
G03F 7/26
H01L 21/027

(21)Application number : 07-040523

(22)Date of filing : 28.02.1995

(71)Applicant : TOKYO OHKA KOGYO CO LTD

(72)Inventor : SATO MITSURU
OMORI KATSUMI
ISHIKAWA KIYOSHI
IGUCHI ETSUKO
NAKAYAMA TOSHIMASA

(30)Priority

Priority number : 06165663 Priority date : 18.07.1994 Priority country : JP

(54) BASE MATERIAL FOR LITHOGRAPHY AND MULTILAYERED RESIST MATERIAL USING HEAT

(57)Abstract:

PURPOSE: To provide such a material that a resist pattern of square cross section having high resolution and high aspect ratio can be formed in which reflected light from a substrate can sufficiently be suppressed, no intermixing layer is produced, no notching is caused and excellent dimensional accuracy for the mask pattern is obtd.

CONSTITUTION: The base material for lithography contains (a) a triazine compd. having at least two crosslinkable functional groups, (b) material having high absorbance, and (c) alkali-insoluble acryl resin, at need. The multilayered resist material is obtd. by successively forming a layer of this base material and a resist layer on a substrate. It is preferable that the component (a) is a triazine compd. having hydroxyl groups and/or alkoxyl groups, and especially melamine or guanamine with substitution of methylol groups and/or alkoxymethyl groups. The component (b) is a benzophenone, diphenylsulfone, or diphenylsulfoxide material, and the component (c) is an acryl resin having glycidyl groups.

LEGAL STATUS

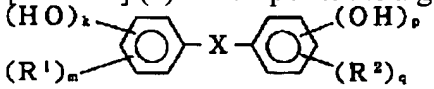
[Date of request for examination]	09.04.1997
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	2953562
[Date of registration]	16.07.1999
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

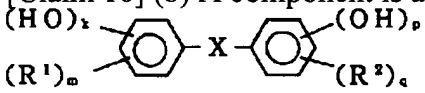
CLAIMS

[Claim(s)]
[Claim 1] (a) Substrate material for lithography characterized by containing a triazine compound and (b) high extinction nature matter with at least two arch-forming nature functional groups.
[Claim 2] (a) Substrate material for lithography characterized by containing a triazine compound, (b) high extinction nature matter, and (c) alkali insolubility acrylic resin with at least two arch-forming nature functional groups.
[Claim 3] (a) Substrate material for lithography according to claim 1 or 2 which is the triazine compound in which a component has hydroxyl, an alkoxyl group, or its both.
[Claim 4] (a) Substrate material for lithography according to claim 3 which is a melamine or guanamine by which a component was replaced by methylol radical, alkoxy methyl group, or its both.
[Claim 5] (b) Substrate material for lithography according to claim 1 or 2 whose component is the benzophenone system high extinction nature matter.
[Claim 6] Substrate material for lithography according to claim 5 whose benzophenone system high extinction nature matter is a polyhydroxy benzophenone.
[Claim 7] (b) A component is a general formula. [Formula 1]



(-SO- or -SO2-, and R1 and R2 X in a formula) It is a hydrogen atom, a halogen atom, or a low-grade alkyl group, respectively, and even if they are mutually the same, you may differ. k, m, p, and q Are the integer of 1-3, respectively, and the relation between k+m=5 and p+q=5 is filled. the case where there is two or more R1 -- every -- the case where you may differ even if R1 is the same, and there is two or more R2 -- every -- even if R2 is the same -- differing -- **** -- the substrate material for lithography according to claim 1 or 2 which is the compound expressed.
[Claim 8] (b) Substrate material for lithography according to claim 7 whose component is a screw (polyhydroxy phenyl) sulfone or a screw (polyhydroxy phenyl) sulfoxide.
[Claim 9] (c) Substrate material for lithography according to claim 2 which is acrylic resin in which a component has a glycidyl group.
[Claim 10] a substrate top -- (a) -- a multilayer-resist material which prepares a resist layer and changes on a substrate material layer which applied a substrate material solution for lithography which dissolved a triazine compound and (b) high extinction nature matter with at least two arch-forming nature functional groups in an organic solvent, and the (a) component and the (b) component were made to construct a bridge, and was formed.
[Claim 11] a substrate top -- (a) -- a multilayer-resist material which prepares a resist layer and changes on a substrate material layer for lithography which applied a substrate material solution for lithography which dissolved a triazine compound, (b) high extinction nature matter, and (c) alkali insolubility acrylic resin with at least two arch-forming nature functional groups in an organic solvent, and the (a) component, the (b) component, and the (c) component were made to construct a bridge, and was formed.

[Claim 12] (a) A multilayer-resist material according to claim 10 or 11 which is the triazine compound in which a component has hydroxyl, an alkoxyl group, or its both.
[Claim 13] (a) A multilayer-resist material according to claim 12 which is melanin or guanamine by which a component was replaced by methylol radical, alkoxy methyl group, or its both.
[Claim 14] (b) A multilayer-resist material according to claim 10 or 11 whose component is the benzophenone system high extinction nature matter.
[Claim 15] A multilayer-resist material according to claim 14 whose benzophenone system high extinction nature matter is a polyhydroxy benzophenone.
[Claim 16] (b) A component is a general formula. [Formula 2]



(-SO- or -SO2-, and R1 and R2 X in a formula) It is a hydrogen atom, a halogen atom, or a low-grade alkyl group, respectively, and even if they are mutually the same, you may differ. k, m, p, and q Are the integer of 1-3, respectively, and the relation between k+m=5 and p+q=5 is filled. the case where there is two or more R1 -- every -- the case where you may differ even if R1 is the same, and there is two or more R2 -- every -- even when R2 is the same -- differing -- **** -- the multilayer-resist material according to claim 10 or 11 which is the compound expressed.
[Claim 17] (b) A multilayer-resist material according to claim 16 whose component is a screw (polyhydroxy phenyl) sulfone or a screw (polyhydroxy phenyl) sulfoxide.
[Claim 18] (c) A multilayer-resist material according to claim 11 which is acrylic resin in which a component has a glycidyl group.

[Translation done.]

* NOTICES *

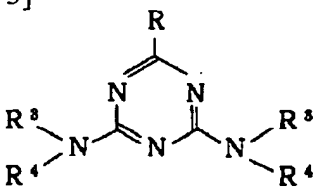
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the multilayer-resist material using the new substrate material for lithography and new it. If it says in more detail, this invention relates to the substrate material for lithography excellent in the large heat crosslinking reaction nature of an aspect ratio, and the multilayer-resist material using this substrate material, when giving a resist pattern faithful to a mask pattern, without fully being able to control the reflected light from a substrate and producing INTAMIKISHINGU, notching, etc.
[0002]
[Description of the Prior Art] When using conventionally the substrate which has high reflexibility films, such as an aluminum film and a tungsten silicide film, and the substrate which has a level difference in a lithography process, the fidelity of the resist pattern to a mask pattern falling, and producing deterioration of dimensional accuracy, the local distortion of a resist pattern, and the so-called notching by the scattered reflection from the effect and the substrate of a standing wave, is known.
[0003] Moreover, although short wavelength-ization of the radiation for image formation progresses with buildup of the degree of integration of a semiconductor device and the lithography using i line (365nm), far ultraviolet rays, and an excimer laser is becoming in use in recent years, when the radiation of such short wavelength is used, there is an inclination for the reflected light to become large also in an ordinary substrate not only like the substrate which does not have a high reflexibility film like an aluminum film or a tungsten silicide film, and the substrate which has a level difference but silicon oxide.
[0004] therefore, ARC (Anti-Reflective Coating) which prepares an antireflection film between a substrate and a resist layer in order to control deterioration of the dimensional accuracy of the resist pattern to the mask pattern by the reflected light, and notching in recent years -- law attracts attention and the antireflection film (substrate material) of former versatility is proposed.
[0005] For example, although what prepared the antireflection film which added the ultraviolet ray absorbent between the substrate and the resist layer is proposed (JP,59-93448,A), this antireflection film has the defect of the adhesion of a resist layer or an antireflection film being low, and producing exfoliation or generating residue Society for Cutting Up Men, in order to have to use a polyamine acid and a polybutene sulfonic acid as a resinous principle.
[0006] In order to improve such a defect, a diphenylamine derivative and a melamine derivative are condensed under existence of an acid catalyst. the pattern formation material (JP,3-67261,B --) which blended the high extinction nature matter which has absorbing power in the sensitization property wavelength region of the sensitization component of a resist layer with the resin obtained JP,63-138353,A and the substrate material (JP,6-35201,A) which blended the ultraviolet ray absorbent with copolymer of glycidyl methacrylate and methyl methacrylate, The antireflection film (JP,6-69124,A) using Pori (alpha-cyanoacetic-acid vinyl) or the antireflection film (JP,6-75378,A) using the compound which has a maleic anhydride and an ethylene nature partial saturation double bond is proposed.

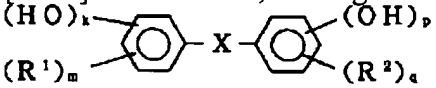
[0007] However, since they will produce INTAMIKISHINGU between a resist layer, and the acid-resisting layer and substrate layer which are prepared on it if these things have the inadequate compatibility of an ultraviolet ray absorbent and a resinous principle, a limit is in the amount of the ultraviolet ray absorbent which can be blended and the critical mass is exceeded, they have the defect that the dimensional accuracy of the mask pattern which cannot fully heighten the acid-resisting effect upwards and can respond to detailed-ization of a semiconductor device is not acquired. Furthermore, although it was desirable to enlarge the ratio of the etch rate of the substrate material to the etch rate of a resist layer, i.e., an aspect ratio, in order to have raised the fidelity to working capacity or a mask pattern, these substrate material was not able to enlarge this aspect ratio enough.
[0008] Moreover, deep using polysulfone or a polyurea sulfone The antireflection film for UV is proposed (U.S. Pat. No. 5,234,990 description). However, when a resist pattern is formed using such an antireflection film, in the interface of a resist and an antireflection film (resist bottom portion), there is a possibility that an undercut phenomenon may happen, as a result the phenomenon of the failure by the pattern may arise.
[0009] Furthermore, the antireflection film containing heat cross linking agents, such as phenol nature resin, melamine-formaldehyde resin, etc., such as novolak resin, is proposed (JP,6-118631,A). However, since novolak resin is contained, this reflective film has the too strong etching-proof nature of the antireflection film itself, and in case it removes an antireflection film by dry etching, it has the problem that ****** of the resist pattern formed in that upper layer also becomes large, and an aspect ratio becomes small. Furthermore, although the melamine-formaldehyde resin contained as a heat cross linking agent has the arch-forming nature functional group, it does not fit manufacture of the semiconductor device as which heat crosslinking reaction must be carried out at an elevated temperature for a long time in case heat crosslinking reaction nature makes an antireflection film form rather than is enough, therefore a high throughput is required.
[0010]
[Problem(s) to be Solved by the Invention] This invention is made for the purpose of offering the substrate material for lithography excellent in the large heat crosslinking reaction nature of an aspect ratio, and the multilayer-resist material using this substrate material, when giving a faithful resist pattern to a mask pattern, without being able to solve the problem which such conventional technology has, fully being able to control the reflected light from a substrate, and producing INTAMIKISHINGU and notching.
[0011]
[Means for Solving the Problem] A triazine compound which has the functional group which can form bridge formation with heating as a result of repeating research variously about amelioration of substrate material for lithography, in order that this invention persons may attain said object, If substrate material which made high extinction nature matter contain is used, the reflected light from a substrate can fully be controlled. That an aspect ratio can be enlarged if producing neither INTAMIKISHINGU nor notching and giving a faithful resist pattern to a mask pattern and this are made to contain alkali insolubility acrylic resin further Moreover, a header, Based on this knowledge, it came to make this invention.
[0012] namely, this invention -- (a) -- a triazine compound with at least two arch-forming nature functional groups -- (b) High extinction nature matter and substrate material for lithography characterized by containing (c) alkali insolubility acrylic resin by case, A substrate material solution for lithography which dissolved the (c) component in an organic solvent by the above-mentioned (a) component, the (b) component, and case on a substrate is applied to a list. (a) A multilayer-resist material which prepares a resist layer and changes on a substrate material layer for lithography which the (c) component used by component, the (b) component, and case was made to construct a bridge, and was formed is offered.
[0013] A triazine compound used as a (a) component in this invention has two or more functional groups which can form bridge formation between the (b) component which are selves or is used together by heating, the (c) component, or its both. As an example of such an arch-forming nature functional

group, a methylol radical and an alkoxy methyl group can be mentioned.
[0014] As an example of a triazine compound used as this component, it is a general formula. [Formula 3]



(I)

The substitute melamine or substitute guanamine expressed with (R in a formula is a hydrogen atom, an alkyl group, an aralkyl radical, an aryl group, or three R4 -NR(s), are whether R3 and R4 are mutually the same and a different thing, and at least two in 4-6 R3 and R4 which exist in a molecule are a methylol radical or an alkoxy methyl group although a hydrogen atom, a methylol radical, and an alkoxy methyl group are shown, respectively) can be mentioned. These may exist as a dimer or a trimer again, and the number of the methylol radical per triazine ring or alkoxy methyl groups has desirable or more an average of 3 less than six range.
[0015] Such a triazine compound can be easily manufactured making a melamine or guanamine react with formalin, and methylol-izing it in a boiling water, according to the well-known method, or by making lower alcohol react to this further, and alkoxyl-izing. The melamine replaced by the melamine and an average of 5.8 methoxymethyl radicals which were replaced by an average of 3.7 methoxymethyl radicals can come to hand in these compounds as commercial item Mx-750 and Mw-30 (all are Sanwa chemical company make), respectively.
[0016] Next, the high extinction nature matter used as a (b) component of this invention High absorbing power is shown to the light in the sensitization property wavelength region of the sensitization component in the resist layer prepared on the substrate material of this invention. That what is necessary is just what can prevent the scattered reflection by the level difference on the standing wave produced by the echo from a substrate, or the front face of a substrate, although used as a component of substrate material or an antireflection film until now, it can be used from inside, being able to choose it as arbitration. As such high extinction nature matter, although a SARISHI rate system, a benzophenone system, a benzotriazol system, the cyanoacrylate system, the azo system, the polyene system, the anthraquinone system, etc. are known, for example In these, a polyhydroxy benzophenone, a point with especially sufficient compatibility [as opposed to the (a) component or a solvent in a 2, 2', 4, and 4'-tetra-hydroxy benzophenone], It is advantageous at the point of having a reaction facilitatory effect to the heat bridge formation of a point and the (a) component which does not produce INTAMIKISHINGU, the point of excelling in the extinction engine performance to the light of the wavelength below i line (365nm), and the point of excelling in heat cross-linking with the (a) component further.
[0017] Furthermore, it is a general formula as this (b) component. [Formula 4]



(II)

(-SO- or -SO2-, and R1 and R2 X in a formula) It is a hydrogen atom, a halogen atom, or a low-grade alkyl group, respectively, and even if they are mutually the same, you may differ. k, m, p, and q the case where it is the integer of 1-3, respectively, and the relation between k+m=5 and p+q=5 is filled, and there is two or more R1 -- every -- the case where you may differ even if R1 is the same, and there is two or more R2 -- every -- even when R2 is the same -- differing -- **** -- the compound expressed can also be used.
[0018] In the compound expressed with this general formula (II), as an example in case X is -SO2- A screw (2, 4-dihydroxy phenyl) sulfone, a screw (3, 4-dihydroxy phenyl) sulfone, A screw (3, 5-dihydroxy phenyl) sulfone, a screw (3, 6-dihydroxy phenyl) sulfone, A screw (4-hydroxyphenyl)

sulfone, a screw (3-hydroxyphenyl) sulfone, A screw (2-hydroxyphenyl) sulfone, a screw (3, 5-dimethyl-4-hydroxyphenyl) sulfone, etc. are mentioned, and as an example in the case of being -SO- A screw (2, 3-dihydroxy phenyl) sulfoxide, a screw (5-chloro-2, 3-dihydroxy phenyl) sulfoxide, A screw (2, 4-dihydroxy phenyl) sulfoxide, a screw (2, 4-dihydroxy-6-methylphenyl) sulfoxide, A screw (5-chloro-2, 4-dihydroxy phenyl) sulfoxide, A screw (2, 5-dihydroxy phenyl) sulfoxide, a screw (3, 4-dihydroxy phenyl) sulfoxide, A screw (3, 5-dihydroxy phenyl) sulfoxide, a screw (2, 3, 4-trihydroxy phenyl) sulfoxide, A screw (2, 3, 4-trihydroxy-6-methylphenyl)-sulfoxide, A screw (5-chloro - 2, 3, 4-trihydroxy phenyl) sulfoxide, a screw (2, 4, 6-trihydroxy phenyl) sulfoxide, a screw (5-chloro - 2, 4, 6-trihydroxy phenyl) sulfoxide, etc. are mentioned.

[0019] deep of the substrate material obtained by using such a sulfone compound and a sulfoxide compound An aspect ratio also becomes large, while the permeability to UV (especially 248nm) is low and the good upper resist pattern is obtained.

[0020] In these compounds, it has a hydroxyl group at least in p- to the location of X. And the thing of symmetry structure, For example, a screw (2, 4-dihydroxy phenyl) sulfone, a screw (4-hydroxyphenyl) sulfone, A screw (3, 5-dimethyl-4-hydroxyphenyl) sulfone, a screw (2, 4-dihydroxy phenyl) sulfoxide, A screw (2, 4-dihydroxy-6-methylphenyl) sulfoxide, A screw (5-chloro-2, 4-dihydroxy phenyl) sulfoxide, A screw (2, 3, 4-trihydroxy phenyl) sulfoxide etc. Heat crosslinking reaction nature is good, and is desirable, and heat crosslinking reaction nature has a screw (4-hydroxyphenyl) sulfone and an especially high screw (2, 4-dihydroxy phenyl) sulfoxide, and INTAMIKISHINGU does not occur but it is suitable. These high extinction nature matter may be used independently, respectively, and two or more sorts may be combined and it may be used.

[0021] The alkali insolubility acrylic resin of the (c) component used by the case in this invention Glycidyl (meta) acrylate, such as glycidyl acrylate and glycidyl methacrylate, It is the polymer obtained from raw material monomers, such as acrylic-acid (meta) alkyls, such as a methyl acrylate, an ethyl acrylate (meta), and acrylic-acid (meta) propyl. (Meta) As such a polymer, weight average molecular weight, for example 10,000-200,000, The copolymer of the poly glycidyl (meta) acrylate, the poly methyl (meta) acrylate, the poly ethyl (meta) acrylate, glycidyl (meta) acrylate, and methyl (meta) acrylate which are in the range of 20,000-100,000 preferably etc. is mentioned. Also especially in these, since the substrate material for 2:8 thru/or 8:2, and the lithography that the copolymer of the range of 3:7 thru/or 7:3 is not preferably generated by the INTAMIKISHINGU layer, but is high aspect ratios is obtained, the weight ratio of glycidyl methacrylate and methyl methacrylate is desirable.

[0022] The manufacturing method of this acrylic resin is as follows. That is, it is made to dissolve in halogenated hydrocarbon, such as aromatic hydrocarbon, such as ketones, such as a twice [1 - 5 weight] as many organic solvent, for example, a methyl ethyl ketone, as this and an acetone, benzene, toluene, and ethylbenzene, chloroform, and a carbon tetrachloride, etc. to the above-mentioned sum total weight of a raw material monomer, azobisisobutyronitril, azobisvaleronitrile, benzoyl peroxide, lauryl peroxide, etc. are usually added 0.05 to 0.5% of the weight to the sum total weight of a raw material monomer as a polymerization initiator, and it is because it agitates in nitrogen-gas-atmosphere mind. Usually, although reaction temperature is chosen at 50-80 degrees C and reaction time is chosen in 3 - 12 hours, the class of polymer made into the object and weight average molecular weight can adjust suitably.

[0023] Thus, after adding the obtained polymer into alcohol, such as a methanol and ethanol, and depositing it, what carried out reduced pressure drying is preferably used as the above-mentioned acrylic resin.

[0024] (a) the blending ratio of coal of a component and the (b) component -- the (a) component 100 weight section -- receiving -- the (b) component 10 - the 300 weight sections -- the range of the 20 - 200 weight section is preferably desirable. the case where the (c) component is used by the case -- the total quantity 100 weight section of the (a) component and the (b) component -- receiving -- the 1 - 400 weight section -- the range of the 5 - 300 weight section is preferably desirable. When there are too few these rates than the above-mentioned range, even if many [the target absorbance is not obtained, notching arises, or the target aspect ratio is not obtained and / too], an INTAMIKISHINGU layer arises.

[0025] As for the substrate material for lithography, in this invention, it is desirable to dissolve in a suitable solvent and to use the above-mentioned (a) component, the (b) component, and the (c) component used by the case in the form of a solution.
[0026] As such a solvent, for example An acetone, a methyl ethyl ketone, cyclopentanone, A cyclohexanone, methyl amyl ketone, methyl isoamyl ketone, Ketones, such as a 1, 1, and 1-trimethyl acetone, ethylene glycol, Ethylene glycol mono-acetate, diethylene-glycol, or diethylene-glycol mono-acetate, Propylene glycol and propylene glycol mono-acetate or these monomethyl ether, Polyhydric alcohol, such as the monoethyl ether, the monopropyl ether, the monobutyl ether, or the monophenyl ether, and the derivative of those, Ester, such as cyclic ether like dioxane, and ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, pyruvic-acid ethyl, 3-methoxy methyl propionate, 3-ethoxy ethyl propionate, can be mentioned. These may be used independently, and may mix and use two or more sorts.
[0027] moreover, to the substrate material for lithography of this invention The acetic acid used as the accelerator of the crosslinking reaction of the additive which is furthermore compatible if needed, for example, a triazine compound with at least two arch-forming nature functional groups of the (a) component, Organic acids, such as oxalic acid, a maleic acid, ortho hydroxybenzoic acid, 3, 5-dinitro benzoic acid, 2, 6-dihydroxybenzoic acid, and SAX (Mitsui Toatsu Chemicals, Inc. make), can be added in less than 5% of the weight of the range to the solid content of substrate material.
[0028] Moreover, improvement in spreading nature and the surfactant for striae SHON prevention can be added. as such a surfactant -- Sir -- chlorofluocarbon SC-103, SR-100 (Asahi Glass Co., Ltd. make), EF-351 (northeast fertilizer company make), and Fluorad Fc- fluorochemical surfactants, such as 431, Fluorad Fc-135, Fluorad Fc-98, Fluorad Fc-430, and Fluorad Fc-176 (Sumitomo 3 M company make), are mentioned, and the addition can be added in less than 2000 ppm to the solid content of substrate material.
[0029] The substrate material for lithography of this invention can use any resists regardless of a negative mold and a positive type. The positive resist which contains ** naphthoquinonediazide compound and novolak resin as such a resist, ** The positive resist containing the compound which generates an acid by exposure, the compound with which it decomposes an acid and the solubility over an alkali aqueous solution increases, and alkali fusibility resin, ** Although the negative resist containing the positive resist containing the alkali fusibility resin which has the radical on which the compound and acid which generate an acid by exposure decompose into, and the solubility over an alkali aqueous solution increases, the compound which generates an acid by ** exposure, a cross linking agent, and alkali fusibility resin etc. is mentioned It is not limited to these.
[0030] First, in order to produce the multilayer-resist material of this invention using this substrate material for lithography, after carrying out revolution spreading of the substrate material solution which dissolved in the organic solvent which described this substrate material above, and was prepared with a spinner etc., and the substrate material layer of 0.05-0.3-micrometer thickness is formed on a suitable substrate. [the temperature of 100-300 degrees C] The substrate material of this invention produces crosslinking reaction at this temperature, and it becomes insoluble to an alkali solution, and is hard coming to form an INTAMIKISHINGU layer with the upper resist layer. Thus, what is necessary is to carry out revolution spreading of the resist layer with a spinner etc., to dry and just to prepare a resist layer on this, after forming a substrate material layer.
[0031] Thus, it glares, exposing ultraviolet rays through a necessary mask pattern to the resist layer of the obtained multilayer-resist material using the light source which emits light, for example, a low pressure mercury lamp, a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, the arc light, a xenon lamp, an excimer laser stepper, etc., or scanning an electron ray. Next, if the dipping of this is carried out to a developer, for example, an alkaline aqueous solution like a 1 - 10-% of the weight tetramethylammonium hydroxide aqueous solution, it is a positive type and an exposure portion is a negative mold, dissolution clearance of the unexposed portion will be carried out selectively, and a resist pattern faithful to a mask pattern will be formed.

[0032] Subsequently, a substrate material layer is patternized by the dry etching method using chlorine gas by using a resist pattern as a mask. In addition, although it is already a well-known method to silanize the upper resist layer in order to make an aspect ratio high, you may carry out combining this silanizing processing. Although it can carry out as one example of such silanizing processing by exposing this resist layer that carried out pattern NINGU for 1 - 60 minutes at the temperature of the range of 30-100 degrees C to the steam of sililation reagents, such as hexamethyldisilazane, a hexa methyl SHIKUROTORI silazane, and other polyfunctional silazanes, after carrying out pattern NINGU of the upper resist, it is not limited to these.
[0033]
[Effect of the Invention] While the substrate material for lithography of this invention is excellent in the large heat crosslinking reaction nature of an aspect ratio, and fully being able to control the reflected light from a substrate, there being no generating of an INTAMIKISHINGU layer, and notching's not happening but excelling in the dimensional accuracy over a mask pattern, a cross section can give the resist pattern of high resolution and a high aspect ratio with a rectangle.
[0034] It is the compound replaced by an average of 3.7 methoxy methylol radicals per example of manufacture 1 melamine ring. MX-750 (Sanwa chemical company make) --g [100], 2, 2', 4, and 4'-tetra-hydroxy benzophenone 100g and Fc-430 (Sumitomo 3 M company make --) 1000 ppm of fluorochemical surfactants were dissolved in propylene-glycol-monomethyl-ether acetate 2700g, and the solution of substrate material was obtained by filtering using the membrane filter whose aperture is 0.2 micrometers.
[0035] Example of manufacture 2 glycidyl-methacrylate 100g and methyl methacrylate 100g are dissolved in methyl-ethyl-ketone 200g, and it was made to react at 60 degrees C for about 7 hours, adding N and N'-azobisisobutyronitril 2g and agitating in nitrogen-gas-atmosphere mind. The reactant was added into 1l. of methanols after reaction termination, the polymer was deposited, and reduced pressure drying of this polymer was carried out under the room temperature. The yield of a polymer was 150g and weight average molecular weight was 60,000. It is the compound replaced by this polymer of 91g, and an average of 5.8 methoxy methylol radicals per melamine ring. Mw-30 (Sanwa chemical company make) --g [27.2], 2, 2', 4, and 4'-tetra-hydroxy benzophenone 72.8g -- SAX(Mitsui Toatsu Chemicals, Inc. make) 9.0g and Fc-430 (Sumitomo 3 M company make --) 1000 ppm of fluorochemical surfactants were dissolved in propylene-glycol-monomethyl-ether acetate 2600g, and the solution of substrate material was obtained by filtering using the membrane filter whose aperture is 0.2 micrometers.
[0036] Same polymer [as what was used in the example 2 of example of manufacture 3 manufacture]g [100] and 2, 2', 4, and 4'-tetra-hydroxy benzophenone 80g, and Fc-430 (Sumitomo 3 M company make, fluorochemical surfactant) 1000ppm were dissolved in propylene-glycol-monomethyl-ether acetate 2400g, and the solution of substrate material was obtained by filtering using the membrane filter whose aperture is 0.2 micrometers.
[0037] Same polymer [as what was used in the example 2 of example of manufacture 4 manufacture]g [100] and 2, 2', 4, and 4'-tetra-hydroxy benzophenone 30g, and Fc-430 (Sumitomo 3 M company make, fluorochemical surfactant) 1000ppm were dissolved in propylene-glycol-monomethyl-ether acetate 2400g, and the solution of substrate material was obtained by filtering using the membrane filter whose aperture is 0.2 micrometers.
[0038] MX-750(Sanwa chemical company make) 5g which is the compound replaced by an average of 3.7 methoxy methylol radicals per example of manufacture 5 melamine ring, screw (4-hydroxyphenyl) sulfone 5g, and Fc-430 (Sumitomo 3 M company make, fluorochemical surfactant) 1000ppm were dissolved in propylene-glycol-monomethyl-ether acetate 90g, and the solution of substrate material was obtained by filtering using the membrane filter whose aperture is 0.2 microns.
[0039] MX-750(Sanwa chemical company make) 5g which is the compound replaced by an average of 3.7 methoxy methylol radicals per example of manufacture 6 melamine ring, screw (2, 4-dihydroxy phenyl) sulfoxide 5g, and Fc-430 (Sumitomo 3 M company make, fluorochemical surfactant) 1000ppm were dissolved in propylene-glycol-monomethyl-ether acetate 90g, and the solution of substrate material

was obtained by filtering using the membrane filter whose aperture is 0.2 microns.
[0040] 5g (Mw=5,000) of phenol novolak resin obtained by condensing example of manufacture 7 (antireflection film indicated by JP,6-118631,A) phenol, and formaldehyde according to an acid catalyst, Mw-30HM(Sanwa chemical company make)2.5g which is a hexamethoxy methyl melamine, and Fc-430 (Sumitomo 3 M company make --) 1000 ppm of fluorochemical surfactants were dissolved in propylene-glycol-monomethyl-ether acetate 70g, and the solution of substrate material was obtained by filtering using the membrane filter whose aperture is 0.2 microns.
[0041]
[Example] Next, although an example explains this invention to details further, this invention is not limited at all by these examples.
[0042] On the example 1 silicon wafer, spinner spreading of the solution of the substrate material obtained in the example 1 of manufacture was carried out, desiccation was performed for 90 seconds at 90 degrees C, subsequently it could be burned for 5 minutes at 180 degrees C, and the substrate material layer with a thickness of about 0.15 micrometers was formed. Next, spinner spreading of TSMR-iP3300 (TOKYO OHKA KOGYO CO., LTD. make) which is the positive type photoresist which consists of a naphthoquinonediazide compound and novolak resin intrinsically was carried out on the substrate material layer, at 90 degrees C, it could be burned for 90 seconds and the resist layer of 1.00 micrometers of thickness was formed. This resist layer was exposed through the mask pattern using NSR-1755i9C (NIKON CORP. make), subsequently exposure afterbaking processing (PEB) was performed for 90 seconds at 110 degrees C, negatives were developed in the tetramethylammonium hydroxide aqueous solution 2.38% of the weight, and the resist pattern was formed.
[0043] Next, dry etching was performed at 30mTorr, output 150W, and the temperature of 20 degrees C by making chlorine gas into etchant using plasma etching system TUE-1102 (TOKYO OHKA KOGYO CO., LTD. make). It was 1.91 when asked for the aspect ratio in that case. Moreover, when the following method estimated the cross-section configuration of formed INTAMIKISHINGU, notching, and the upper resist, it was O about all properties.
[0044] In example 2 example 1, it evaluated about an aspect ratio, INTAMIKISHINGU, notching, and a cross-section configuration like the example 1 except having replaced the used substrate material with what was prepared in the example 2 of manufacture. The result is shown in a table 1.
[0045] In example of comparison 1 example 1, it evaluated about an aspect ratio, INTAMIKISHINGU, notching, and a cross-section configuration like the example 1 except having replaced the used substrate material with what was prepared in the example 3 of manufacture. The result is shown in a table 1.
[0046] In example of comparison 2 example 1, it evaluated about an aspect ratio, INTAMIKISHINGU, notching, and a cross-section configuration like the example 1 except having replaced the used substrate material with what was prepared in the example 4 of manufacture. The result is shown in a table 1.
[0047] On the example 3 silicon wafer, spinner spreading of the solution of the substrate material obtained in the example 1 of manufacture was carried out, desiccation processing was performed for 90 seconds at 90 degrees C, subsequently it could be burned for 5 minutes at 180 degrees C, and the substrate material layer with a thickness of about 0.15 micrometers was formed. Next, spinner spreading of THMR-iN200 (TOKYO OHKA KOGYO CO., LTD. make) which consists of an acid generator, a cross linking agent, and alkali fusibility resin intrinsically was carried out on the substrate material layer, at 110 degrees C, it could be burned for 90 seconds and the resist layer of 1.00 micrometers of thickness was formed. This resist layer was exposed through the mask pattern using NSR-1755i9C (NIKON CORP. make), subsequently exposure afterbaking processing (PEB) was performed for 90 seconds at 100 degrees C, negatives were developed in the tetramethylammonium hydroxide aqueous solution 2.38% of the weight, and the resist pattern was formed.
[0048] The following dry etching processings were performed like the example 1, and were evaluated about an aspect ratio, INTAMIKISHINGU, notching, and a cross-section configuration. The result is shown in a table 1.
[0049] In example 4 example 3, it evaluated about an aspect ratio, INTAMIKISHINGU, notching, and a cross-section configuration like the example 3 except having replaced the used substrate material with

what was prepared in the example 2 of manufacture. The result is shown in a table 1.
[0050] In example of comparison 3 example 3, it evaluated about an aspect ratio, INTAMIKISHINGU, notching, and a cross-section configuration like the example 3 except having replaced the used substrate material with what was prepared in the example 3 of manufacture. The result is shown in a table 1.
[0051] In example of comparison 4 example 3, it evaluated about an aspect ratio, INTAMIKISHINGU, notching, and a cross-section configuration like the example 3 except having replaced the used substrate material with what was prepared in the example 4 of manufacture. The result is shown in a table 1. In addition, the following methods estimated each physical properties in each example and the example of a comparison.
[0052] (1) Aspect ratio; when the etching rate of the upper resist after desiccation was set to X on the etching conditions of an example 1 and the etching rate of the substrate material after desiccation was set to Y, in quest of Y/X, it considered as the aspect ratio.
[0053] (2) INTAMIKISHINGU; the cross section of a sample was observed with the scanning electron microscope, and the case where O and an INTAMIKISHINGU layer were formed in the case where the INTAMIKISHINGU layer is not formed in the boundary of the upper resist and substrate material was made into x.
[0054] (3) Notching; heat-treatment after the exposure indicated in the example 1 or the example 3 and exposure, development, and a series of processings of dry etching were performed through the 0.40-micrometer mask pattern, the several straight-lines-like resist pattern made to form on the flat surface of a sample at parallel was observed, and the case where distortion was produced for the case where deformation is not accepted, in O and each straight line was made into x.
[0055] (4) Cross-section configuration; heat-treatment after the exposure indicated in the example 1 or the example 3 and exposure and a series of processings of development were performed through the 0.40-micrometer mask pattern, the cross section of a resist pattern was observed with the scanning electron microscope, the case where an edge was sharp was made as O, and the case where it was round was made into x.
[0056]
[A table 1]

実施例及び比較例	アスペクト比	インターミキシング	ノッチング	断面形状
実施例1	1．91	O	O	O
実施例2	3．10	O	O	O
実施例3	1．56	O	O	O
実施例4	2．53	O	O	O
比較例1	2．40	×	×	×
比較例2	2．51	O	×	×
比較例3	1．95	×	×	×
比較例4	2．05	O	×	×

[0057] On the example 5 silicon wafer, spinner spreading of the solution of substrate material prepared in the example 5 of manufacture was carried out, desiccation was performed for 90 seconds at 90 degrees C, subsequently it could be burned for 90 seconds at 180 degrees C, and the about 0.1-micron substrate material layer in thickness was formed.
[0058] Next, spinner spreading of the DP-007AS (TOKYO OHKA KOGYO CO., LTD. make) which is the chemistry amplification mold positive resist which consists of the polyhydroxy styrene which has intrinsically the substituent which changes to alkali fusibility according to an operation of an acid generator and an acid was carried out on substrate material, it could be burned for 90 seconds at 90 degrees C, and the resist layer of 0.7 microns of thickness was obtained. This resist layer was exposed through the mask pattern using NSR2005Ex8A (NA=0.5, NIKON CORP. make), subsequently exposure afterbaking processing (PEB) was performed for 90 seconds at 110 degrees C, paddle development was carried out for 65 seconds in the tetramethylammonium hydroxide aqueous solution 2.38% of the

weight, and the resist pattern was formed. Consequently, the 0.3-micron line and the space pattern were formed in the shape of a rectangle.
[0059] Next, dry etching was performed at 30mTorr, output 150W, and the temperature of 20 degrees C by making chlorine gas into etching gas using plasma etching system TUE-1102 (TOKYO OHKA KOGYO CO., LTD. make). It was 2.0, when the etching rate of the upper resist layer after desiccation was set to X, the etching rate of the substrate material layer after desiccation was set to Y at that time and the aspect ratio was computed in quest of Y/X. Moreover, the INTAMIKISHINGU layer was not observed when the cross section of a sample was observed with the scanning electron microscope. Furthermore, notching was not observed when observed with the scanning electron microscope also about notching.
[0060] In example 6 example 5, except having replaced with what prepared substrate material in the example 6 of manufacture, like the example 5, the resist pattern was obtained, subsequently etching processing was carried out, and it evaluated about the existence of a cross-section configuration, an aspect ratio, INTAMIKISHINGU, and notching. Consequently, the 0.3-micron line and the space pattern were formed in the shape of a rectangle. An aspect ratio is 2.0 and INTAMIKISHINGU and notching were not observed, either.
[0061] In example of comparison 5 example 5, except having replaced substrate material with CD-7 (BURYUWA Saiensu-Sha make) which is the antireflection film material which dissolves the polymer of a polysulfone system and changes, when the resist pattern was formed like the example 5, only the 0.4-micron line and the space pattern were resolved, the undercut arose at the resist pars basilaris ossis occipitalis, and the failure by the pattern occurred in a certain part. Therefore, etching processing became difficult.
[0062] In example of comparison 6 example 5, except having replaced with what prepared substrate material in the example 7 of manufacture, like the example 5, when the resist pattern was formed, INTAMIKISHINGU arose and it became the resist pattern configuration of skirt length. Therefore, etching processing did not need to be performed.
[0063] In example of comparison 7 example 5, when the resist pattern was formed like the example 5 except having replaced with what prepared substrate material in the example 7 of manufacture, and having replaced baking processing of substrate material with in 5 minutes at 300 degrees C, INTAMIKISHINGU was not produced but the rectangle-like resist pattern was obtained.
[0064] Subsequently, like the example 5, when etched, the aspect ratio was as small as 1.0.

[Translation done.]